

AD A 055102

FOR FURTHER TRAN

A025109

14

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0148

Project NR 064-436

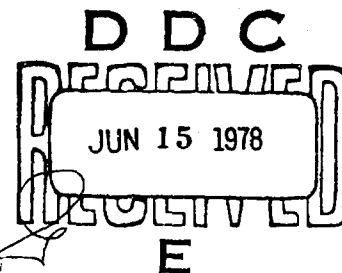
Report No. UCB/AM-78-2

On Thermodynamics and the Nature of the Second Law
for Mixtures of Interacting Continua

by

A. E. Green and P. M. Naghdi

February 1978



Department of Mechanical Engineering

University of California

Berkeley, California

AD No. _____
DDC FILE COPY

Approved for public release; distribution unlimited

On Thermodynamics and the Nature of the Second Law
for Mixtures of Interacting Continua

by

A. E. Green[†] and P. M. Naghdi[‡]

Abstract. This paper, which may be regarded as a continuation of a previous paper on thermodynamics of single phase continua, is concerned with a new approach to thermomechanics of multiphase continua and extends the previous ideas and procedure (Green and Naghdi 1977) to mixtures of interacting continua. In particular, it contains (a) a proposal of a new approach for obtaining restrictions on constitutive equations, (b) an appropriate mathematical statement of the second law for mixtures and (c) the nature of restrictions placed by the latter on constitutive results representing the thermo-mechanical behavior of mixtures with different constituent temperatures. Our point of departure is the introduction of balances of entropy and the use of a single energy equation for the whole mixture as an identity for all motions and all temperature distributions after the elimination of the external fields. This procedure is in contrast to the existing approach in most of the current literature on continuum theories of mixtures based on the use of a Clausius-Duhem type inequality (or similar entropy inequalities) for mixtures. Our interpretation of the second law is similar to that of the previous paper and leads us to postulate an inequality which reflects the fact that for every process associated with a dissipative mixture, a part of the external mechanical work is always converted into heat and this cannot be withdrawn from the mixture as mechanical work. The restriction on the heat conduction vectors is considered separately and is confined to equilibrium cases in which heat flow is steady. Also, a restriction on the specific internal energies is derived when the mixture is in the state of mechanical equilibrium with all its constituents at a common spatially homogeneous temperature. The remainder of the paper deals with the constitutive results and thermodynamic restrictions for inviscid fluids, a fairly detailed consideration of the problem of an incompressible Newtonian viscous fluid flowing through a rigid porous solid whose temperature may be different from that of the fluid, as well as some additional remarks on the implication of the use of an entropy inequality of the Clausius-Duhem type for mixtures as contrasted with the thermodynamic restrictions resulting from the procedure proposed here and from our present interpretation of the second law.

[†]Mathematical Institute, Oxford.

[‡]University of California, Berkeley.

ACCESSION for		
NTIS	White Section	<input checked="" type="checkbox"/>
DDC	Buff Section	<input type="checkbox"/>
UNANNOUNCED		<input type="checkbox"/>
JUSTIFICATION.....		
BY.....		
DISTRIBUTION/AVAILABILITY CODES		
Dist.	AVAIL. and/or SPECIAL	
A		

1. Introduction

The continuum theory of mixtures has been a subject of intensive study in recent years from different points of view; and, at present, there appears to be agreement on the basic thermodynamical equations of the theory. Differences, however, arise over the manner in which a second law of thermodynamics is interpreted for mixtures. A second law is usually employed to place restrictions on constitutive equations; and, even for a single phase continuum, this aspect of the subject is a matter of some controversy. We do not attempt a detailed review of the literature on mixtures, but restrict our attention to references which are relevant to our present development. Briefly, an account of the subject with extensive references prior to 1960 is given by Truesdell and Toupin (10). An alternative approach for mixtures with a single temperature by Green and Naghdi (3,5) is based on different primitive concepts and consequently some of their basic field equations are of different forms from those of Truesdell and Toupin (10). However, it has been shown by Green and Naghdi (5) that the basic equations in the two formulations of the theory are equivalent, although this is not apparent at first sight in the case of some of the equations. For further details and remarks concerning the relationship between the two forms of the theory and the interpretations associated with some of the quantities which occur in the equations, we refer the reader to Green and Naghdi (5,8) and to a recent review articles by Atkin and Craine (1).

The present paper is a companion to the previous work on thermodynamics of single phase continua by Green and Naghdi (9a,b). The latter paper contains a new approach to thermodynamics where, in addition to the usual equations for conservation of mass and momentum, an equation was postulated for balance of entropy and then the equation for balance of energy was required to be satisfied identically for all motions and all temperature distributions after the elimination of the external fields. This resulted in a procedure for obtaining restrictions on

constitutive equations prior to any consideration of a second law of thermodynamics. The particular form of the second law or the law of thermodynamic irreversibility adopted previously ($\underline{9a,b}$) led to an inequality which reflects the fact that for every process associated with a dissipative material, a part of the external mechanical work done is always nonnegative. The restriction on the heat conduction vector, along with a restriction on the internal energy, were discussed previously ($\underline{9a}$) on the basis of the classical concept that heat cannot spontaneously flow from a cold to a hot part of the body; the former restriction was obtained from consideration of the heat flux response in equilibrium cases for which heat flow is steady, while the latter was deduced when the body is in the state of mechanical equilibrium with the temperature field being spatially homogeneous.

In the present paper we extend the ideas and procedure of Green and Naghdi ($\underline{9a,b}$) to mixtures of interacting continua. We begin in §2 by adopting the same conservation laws for mass and momenta as those employed previously by Green and Naghdi ($\underline{5}$), and by Craine, Green and Naghdi ($\underline{2}$). Further, with reference to thermal properties, in §3 we admit for each constituent of the mixture a different field of temperature and a different field of entropy, as well as related thermal fields; and, in parallel with the balances of momenta, we postulate for each constituent a balance of entropy. Next, we recall the balance of energy for the mixture as a whole and, after elimination of external body forces and external entropy supplies, regard the resulting equation as an identity to be satisfied for all thermo-mechanical processes. This procedure should be contrasted with existing methods for mixtures in which use is made of balances of energy (rather than a single energy equation for the mixture as a whole) and in general leads to different constitutive results. For example, in the case of a mixture of ideal fluids with different constituent temperature discussed in §4, our procedure

yields constitutive relations for the partial pressures and diffusive forces which differ from those found by Craine, Green and Naghdi (2), except when all constituents have a common temperature. Inequalities resulting from an appropriate form of a second law for mixtures, as well as restrictions on the heat conduction vectors and internal energies, are discussed in §§3,5,6.

We return to a further discussion of inviscid fluids when the mass of each constituent is separately conserved in §6 and also examine briefly the implication of the second law and restrictions on the heat conduction vectors. The next section (§7) is concerned with some aspects of the flow of an incompressible Newtonian viscous fluid through a porous solid (taken for simplicity as rigid) whose temperature may be different from that of the fluid. Thermodynamic restrictions by the procedure of §3 are obtained for various coefficients of the appropriate linearized constitutive equations, representing small departures from an equilibrium state at which the fluid and the solid have the same constant temperature. Also included in the development of §7 is a brief statement of a uniqueness theorem for the initial boundary-value problem for the determination of the temperature fields in the fluid-rigid solid; and, by way of illustration, a discussion of heat conduction in an infinite stationary rigid porous solid containing an incompressible viscous fluid at rest. We conclude the present paper with some additional remarks in §8 concerning certain features of the present and the previous procedures for studying the thermodynamics of mixtures of interacting continua and also comment on the implication of an entropy inequality of the Clausius-Duhem type for mixtures as contrasted with the thermodynamic restrictions resulting from the procedure proposed here, as well as from our present interpretation of the second law of thermodynamics.

2. Mechanics of mixtures: Summary of basic equations.

Consider a mixture consisting of v finite constituents C_α ($\alpha=1,2,\dots,v$), each regarded as a continuum with material points X^α , and identify the material point X^α of the constituent C_α with its position \tilde{x}^α in some fixed reference configuration. We suppose that the whole of some region of Euclidean space R_0 is simultaneously occupied by all constituents in their reference configurations. A motion of C_α is defined by a sufficiently smooth vector function \tilde{x}^α which assigns position $\tilde{x}^\alpha = \tilde{x}^\alpha(\tilde{x}^\alpha, t)$ to each material point \tilde{x}^α at each instant of time t . In their present configurations at time t , all constituents C_α simultaneously occupy the same region of space R which varies with time and which is bounded by a closed surface ∂R . Similarly, in the present configuration, an arbitrary material part of C_α occupies a portion of the region of space R , which we denote by $P_\alpha (\subseteq R)$ bounded by a closed surface ∂P_α .

Let $\rho_\alpha = \rho_\alpha(\tilde{x}^\alpha, t)$ be the mass density of C_α and designate its velocity vector at time t by

$$\tilde{v}^\alpha = \frac{D^\alpha \tilde{x}^\alpha}{Dt} \quad (2.1)$$

where $D^\alpha()/Dt$ denotes material time derivative holding \tilde{x}^α fixed. At the place \tilde{x} , namely at

$$\tilde{x}^\alpha = \tilde{x} \quad (\alpha=1,2,\dots,v) \quad , \quad (2.2)$$

we define the density ρ of the mixture, the mean (or the barycentric) velocity \tilde{v} of the mixture and the partial diffusion velocities, respectively, by

$$\rho = \sum_{\alpha=1}^v \rho_\alpha \quad , \quad \rho \tilde{v} = \sum_{\alpha=1}^v \rho_\alpha \tilde{v}^\alpha \quad , \quad \tilde{u}^\alpha = \tilde{v}^\alpha - \tilde{v} \quad . \quad (2.3)$$

Since every constituent occupies the same region of space R at each instant of time, at the place \tilde{x} we have

$$\underline{v}^\alpha \cdot \underline{n} = \underline{v} \cdot \underline{n} \quad \text{or} \quad \underline{u}^\alpha \cdot \underline{n} = 0 \quad (\alpha=1,2,\dots,v) \quad \text{on } \partial R, \quad (2.4)$$

where \underline{n} is the outward unit normal to ∂R .

For every material part of C_α occupying a region P_α in the present configuration, we adopt the following equations for conservation of mass, momentum and moment of momentum:

$$\frac{d}{dt} \int_{P_\alpha} \rho_\alpha \, dv = \int_{P_\alpha} m_\alpha \, dv, \quad (2.5)$$

$$\frac{d}{dt} \int_{P_\alpha} \rho_\alpha \underline{v}^\alpha \, dv - \int_{P_\alpha} m_\alpha \underline{v} \, dv = \int_{P_\alpha} (\rho_\alpha \underline{b}^\alpha - \underline{\mu}^\alpha) \, dv + \int_{\partial P_\alpha} \underline{t}^\alpha \, da, \quad (2.6)$$

$$\begin{aligned} \frac{d}{dt} \int_{P_\alpha} \rho_\alpha \underline{x}^\alpha \times \underline{v}^\alpha \, dv - \int_{P_\alpha} m_\alpha \underline{x}^\alpha \times \underline{v} \, dv \\ = \int_{P_\alpha} [\underline{x}^\alpha \times (\rho_\alpha \underline{b}^\alpha - \underline{\mu}^\alpha) + \underline{\lambda}^\alpha] \, dv + \int_{\partial P_\alpha} \underline{x}^\alpha \times \underline{t}^\alpha \, da. \end{aligned} \quad (2.7)$$

In (2.5) to (2.7), m_α is the rate at which mass is supplied to C_α per unit volume,⁺ \underline{b}^α is the external body force per unit mass, $\underline{\mu}^\alpha$ is essentially a measure of diffusive force per unit volume, and $\underline{\lambda}^\alpha$ is the internal body couple per unit volume.

Making the usual continuity assumptions, the conservation laws (2.5) to (2.7) yield the local forms^{*}

$$\frac{\partial \rho_\alpha}{\partial t} + \text{div}(\rho_\alpha \underline{v}^\alpha) = m_\alpha, \quad (2.8)$$

$$\text{div} \underline{T}^\alpha + \rho_\alpha \underline{b}^\alpha - \underline{\mu}^\alpha = m_\alpha \underline{u}^\alpha + \rho_\alpha \underline{f}^\alpha, \quad \underline{t}^\alpha = \underline{T}^\alpha \underline{n}, \quad (2.9)$$

⁺This may include a surface contribution across ∂P_α in the form of the divergence of a vector.

^{*}The detailed development of the conservation laws in the forms (2.5) to (2.7) and their corresponding local forms (2.8) to (2.10) can be found in the papers by Green and Naghdi (5) and by Craine, Green and Naghdi (2). The basic equations (2.8) to (2.10) are equivalent to, but not the same as, those given by Truesdell and Toupin (10). For a discussion of equivalence of the two systems of basic equations, see Green and Naghdi (5). Supplementary discussion on the correlation of existing forms of mixture theories are given in §6 of Green and Naghdi (8).

$$\underline{\Gamma}^\alpha + \underline{T}^\alpha - \underline{T}^{\alpha T} = \underline{0} , \quad (2.10)$$

where all variables are now regarded as functions of \underline{x} and t , div stands for the divergence operator with respect to the place \underline{x} keeping t fixed, \underline{T}^α is the partial stress tensor and $\underline{T}^{\alpha T}$ its transpose, \underline{n} is the outward unit normal to the closed surface ∂P_α , the acceleration vector \underline{f}^α is given by

$$\underline{f}^\alpha = \frac{\partial \underline{v}^\alpha}{\partial t} + \frac{\partial \underline{v}^\alpha}{\partial \underline{x}} \underline{v}^\alpha \quad (2.11)$$

and $\underline{\Gamma}^\alpha$ is the skew tensor corresponding to the axial vector $\underline{\lambda}^\alpha$, so that

$$\underline{\Gamma}^\alpha \underline{u} = \underline{\lambda}^\alpha \times \underline{u} \quad (2.12)$$

for every vector \underline{u} .

We restrict our attention here to a local theory of mixtures in which there is no mass generation within the mixture and in which the internal forces $\underline{\mu}^\alpha$ and the internal couples $\underline{\lambda}^\alpha$ do not give rise to a resultant force and a resultant couple on the mixture as a whole. Then, for material volumes of each constituent C_α which coincide at time t and which occupy parts $P_\alpha = P$ of R , we have

$$\sum_{\alpha=1}^v \int_{P_\alpha} m_\alpha \, dv = 0 , \quad \sum_{\alpha=1}^v \int_{P_\alpha} \underline{\mu}^\alpha \, dv = \underline{0} , \quad \sum_{\alpha=1}^v \int_{P_\alpha} \underline{\lambda}^\alpha \, dv = \underline{0}$$

and we conclude that

$$\sum_{\alpha=1}^v m_\alpha = 0 , \quad \sum_{\alpha=1}^v \underline{\mu}^\alpha = \underline{0} , \quad \sum_{\alpha=1}^v \underline{\lambda}^\alpha = \underline{0} , \quad \sum_{\alpha=1}^v \underline{\Gamma}^\alpha = \underline{0} . \quad (2.13)$$

3. Thermal properties. Thermomechanics of mixtures.

We consider here the thermal properties of the mixture and, for each constituent C_α , introduce first the absolute temperature at each material point by a scalar field $\theta_\alpha = \theta_\alpha(X_\alpha^\alpha, t) > 0$. Along with the temperature, we admit the existence of an external rate of supply of heat $r_\alpha = r_\alpha(X_\alpha^\alpha, t)$ per unit mass and an external rate of surface supply of heat $-\bar{h}_\alpha$ per unit area acting across ∂R . Also, we assume the existence of an internal surface flux of heat $-h_\alpha = -h_\alpha(X_\alpha^\alpha, t; \underline{n})$ per unit area across each surface ∂P_α ; the field h_α , called the partial heat flux and measured per unit area per unit time, assumes the value \bar{h}_α on ∂R . We now define the ratio of heat supply r_α to the temperature θ_α as $s_\alpha = s_\alpha(X_\alpha^\alpha, t)$ and call this the partial external rate of supply of entropy per unit mass. Similarly, we define the ratios of \bar{h}_α and h_α to the temperature θ_α , respectively, as the partial external rate of surface supply of entropy \bar{k}_α per unit area of ∂R and the partial internal surface flux of entropy $k_\alpha = k_\alpha(X_\alpha^\alpha, t; \underline{n})$ per unit area of ∂P_α . These definitions may conveniently be summarized by

$$r_\alpha = \theta_\alpha s_\alpha, \quad \bar{h}_\alpha = \theta_\alpha \bar{k}_\alpha, \quad h_\alpha = \theta_\alpha k_\alpha. \quad (3.1)$$

In addition, for each constituent C_α we assume the existence of a scalar field $\eta_\alpha = \eta_\alpha(X_\alpha^\alpha, t)$ per unit mass, called the partial specific entropy, and a partial internal rate of production of entropy $\xi_\alpha = \xi_\alpha(X_\alpha^\alpha, t)$ per unit mass. The contribution of the latter to the internal rate of production of heat is simply $\theta_\alpha \xi_\alpha$ per unit mass.

We now postulate a balance of entropy for every material volume of C_α occupying a part P_α in the present configuration and write

$$\frac{d}{dt} \int_{P_\alpha} \rho_\alpha \eta_\alpha dv = \int_{P_\alpha} \rho_\alpha (s_\alpha + \xi_\alpha) dv - \int_{\partial P_\alpha} k_\alpha da. \quad (3.2)$$

By usual procedures it can be shown from (3.2) that k_α is linear in \underline{n} , i.e.,

$$k_{\alpha} = \underline{p}^{\alpha} \cdot \underline{n} \quad , \quad (3.3)$$

where \underline{p}^{α} is called the partial entropy flux vector. Then, from (3.1)₃ and (3.3), $h_{\alpha} = \theta_{\alpha} \underline{p}^{\alpha} \cdot \underline{n}$ and we may define the partial heat flux vector \underline{q}^{α} by

$$\underline{q}^{\alpha} = \theta_{\alpha} \underline{p}^{\alpha} \quad . \quad (3.4)$$

Under suitable continuity assumptions and with the use of (3.3), the local equation at the place \underline{x} resulting from (3.2) is

$$\rho_{\alpha} \frac{D^{\alpha} \eta_{\alpha}}{Dt} + m_{\alpha} \eta_{\alpha} = \rho_{\alpha} (s_{\alpha} + \xi_{\alpha}) - \operatorname{div} \underline{p}^{\alpha} \quad , \quad (3.5)$$

where

$$\frac{D^{\alpha} \eta_{\alpha}}{Dt} = \frac{\partial \eta_{\alpha}}{\partial t} + \underline{v}^{\alpha} \cdot \frac{\partial \eta_{\alpha}}{\partial \underline{x}} \quad (3.6)$$

At this point we introduce the first law of thermodynamics or the principle of balance of energy, which states that heat and mechanical energy are equivalent and together they are conserved. We state the law of conservation of energy only for the mixture as a whole. However, the conservation of energy could also be employed for each constituent C_{α} provided full allowance is made for interaction energy from all other constituents, but we do not consider this here.⁺ Thus, with reference to the present configuration and for material volumes which coincide at time t and occupy parts $P_{\alpha} = P$ of R , the balance of energy for the mixture may be stated in the form

⁺This is in contrast with previous work on many temperatures by Green and Naghdi (4) and by Craine, Green and Naghdi (2), where it was necessary to have energy balances for each constituent in order to have sufficient equations for the temperature fields.

$$\sum_{\alpha=1}^v \frac{d}{dt} \int_{P_\alpha} \left(\frac{1}{2} \rho_\alpha \tilde{v}^\alpha \cdot \tilde{v}^\alpha + \rho_\alpha \epsilon_\alpha \right) dv = \sum_{\alpha=1}^v \int_{P_\alpha} (\rho_\alpha \tilde{b}^\alpha \cdot \tilde{v}^\alpha + \rho_\alpha \tilde{r}_\alpha) dv + \sum_{\alpha=1}^v \int_{\partial P_\alpha} (\tilde{t}^\alpha \cdot \tilde{v}^\alpha - h_\alpha) da, \quad (3.7)$$

where $\epsilon_\alpha = \epsilon_\alpha(X^\alpha, t)$ is the partial specific internal energy of the constituent C_α . With the help of (2.8), (2.9), (3.1), (3.4) and (3.5) and under appropriate continuity assumptions, the local energy equation at the place \tilde{x} resulting from (3.7) is

$$\begin{aligned} & - \sum_{\alpha=1}^v \left[\rho_\alpha \left(\frac{D^\alpha \epsilon_\alpha}{Dt} - \theta_\alpha \frac{D^\alpha \eta_\alpha}{Dt} \right) + m_\alpha (\epsilon_\alpha - \theta_\alpha \eta_\alpha) \right] \\ & + \sum_{\alpha=1}^v \left[\tilde{\mu}^\alpha \cdot \tilde{v}^\alpha + \tilde{T}^\alpha \cdot \text{grad } \tilde{v}^\alpha + \frac{1}{2} m_\alpha \tilde{u}^\alpha \cdot \tilde{u}^\alpha \right] \\ & - \sum_{\alpha=1}^v \left[\rho_\alpha \tilde{\xi}_\alpha \theta_\alpha + \tilde{p}^\alpha \cdot \text{grad } \theta_\alpha \right] = 0, \end{aligned} \quad (3.8)$$

where all variables in (3.8) are regarded as functions of \tilde{x} and t and where grad stands for the gradient operator with respect to \tilde{x} keeping t fixed.

Introducing the specific Helmholtz free energy $\psi_\alpha = \psi_\alpha(X^\alpha, t)$ by

$$\psi_\alpha = \epsilon_\alpha - \theta_\alpha \eta_\alpha, \quad (3.9)$$

the energy equation (3.8) may be written in the alternative form

$$\begin{aligned} & - \sum_{\alpha=1}^v \left[\rho_\alpha \left(\frac{D^\alpha \psi_\alpha}{Dt} + \eta_\alpha \frac{D^\alpha \theta_\alpha}{Dt} \right) + m_\alpha \psi_\alpha \right] \\ & + \sum_{\alpha=1}^v \left[\tilde{\mu}^\alpha \cdot \tilde{v}^\alpha + \tilde{T}^\alpha \cdot \text{grad } \tilde{v}^\alpha + \frac{1}{2} m_\alpha \tilde{u}^\alpha \cdot \tilde{u}^\alpha \right] \\ & - \sum_{\alpha=1}^v \left[\rho_\alpha \tilde{\xi}_\alpha \theta_\alpha + \tilde{p}^\alpha \cdot \text{grad } \theta_\alpha \right] = 0. \end{aligned} \quad (3.10)$$

For a given mixture of v constituents having reference mass densities $\rho_{\alpha 0}(X^\alpha)$, the local field equations resulting from the integral forms of the conservation laws involve a set of $12v$ functions. These consist of the deformation functions $\tilde{\chi}^\alpha$ and the temperatures θ_α , i.e.,

$$\{\tilde{x}^\alpha, \theta_\alpha\} \quad (3.11)$$

and the various mechanical and thermal fields, namely

$$\{m_\alpha, \tilde{T}^\alpha, \tilde{\mu}^\alpha, \tilde{\lambda}^\alpha, \eta_\alpha, \epsilon_\alpha, \xi_\alpha, \tilde{p}^\alpha\} \quad (3.12)$$

and

$$\{\tilde{b}^\alpha, s_\alpha\} \quad (3.13)$$

The mass densities ρ_α are not included in (3.12) since, given (3.11), they can be calculated from (2.8). We assume that the fields (3.12) are specified by constitutive equations which may depend on the variables (3.11), their space and time derivatives, as well as the whole history of deformation and temperatures. We then adopt the following procedure in utilizing the conservation laws:

(1) The field equations are assumed to hold for an arbitrary choice of the functions (3.11) including, if required, an arbitrary choice of the space and time derivatives of these functions;

(2) The fields (3.12) are calculated from their respective constitutive equations;

(3) The values of \tilde{b}^α and s_α can then be found from the balances of momenta (2.9) and the balances of entropy (3.5);

(4) The conditions (2.13), the equations (2.10) which are deduced from the balances of moment of momenta and the energy equation (3.10) will be regarded as identities for every choice of (3.11). These will place restrictions on the constitutive equations.

In the current literature on continuum mechanics sometimes certain terminologies such as a thermodynamic process (or simply a process) and an admissible process are employed. In the context of the present paper, the former refers to the specification of 12v functions (3.11) to (3.13) such that they are compatible

with the field equations resulting from the conservation laws (2.5), (2.6), (2.7) and (3.2). In order to specify a thermodynamic process it will suffice to prescribe the 10v functions (3.11) and (3.12) and the remaining 2v functions (3.13) are determined by the field equations resulting from (2.6) and (3.2), which corresponds to (3) above. A thermodynamic process is said to be admissible in the mixture if it is compatible with the constitutive assumption at each point of the mixture for all times, and this corresponds to (1) and (2) in the above procedure. The last step (4) then places restrictions on admissible processes.

Some additional remarks are necessary concerning the entropy equations (3.5). Suppose that the external fields (3.13) have prescribed values and that the constitutive equations have been specified for the set (3.12) in terms of (3.11) and their histories by

$$\begin{aligned} m_\alpha &= \hat{m}_\alpha, \quad T_\alpha = \hat{T}_\alpha, \quad \mu_\alpha = \hat{\mu}_\alpha, \quad \lambda_\alpha = \hat{\lambda}_\alpha, \\ \eta_\alpha &= \hat{\eta}_\alpha, \quad \psi_\alpha = \hat{\psi}_\alpha, \quad \xi_\alpha = \hat{\xi}_\alpha, \quad p_\alpha = \hat{p}_\alpha, \quad \epsilon_\alpha = \hat{\psi}_\alpha + \theta_\alpha \hat{\eta}_\alpha. \end{aligned} \quad (3.14)$$

Then, the requirement that the energy equation (3.10) be identically satisfied leads to the following identity

$$\begin{aligned} - \sum_{\alpha=1}^v \left[\rho_\alpha \left(\frac{D^{\alpha} \hat{\psi}_\alpha}{Dt} + \hat{\eta}_\alpha \frac{D^{\alpha} \theta_\alpha}{Dt} \right) + m_\alpha \hat{\psi}_\alpha \right] \\ + \sum_{\alpha=1}^v \left[\hat{\mu}_\alpha \cdot \underline{v}_\alpha + \hat{T}_\alpha \cdot \text{grad } \underline{v}_\alpha + \frac{1}{2} \hat{m}_\alpha \underline{u}_\alpha \cdot \underline{u}_\alpha \right] \\ - \sum_{\alpha=1}^v \left[\rho_\alpha \hat{\xi}_\alpha \theta_\alpha + \hat{p}_\alpha \cdot \text{grad } \theta_\alpha \right] = 0 \end{aligned} \quad (3.15)$$

relating the response functions in (3.14). Also, the deformation functions and the temperatures must satisfy the differential equations which result from substitution of (3.14) into (2.9)₁ and (3.5). Now, let the constitutive equations be changed to

$$\begin{aligned}
m_\alpha &= \hat{m}_\alpha, \quad T^\alpha = \hat{T}^\alpha, \quad \mu^\alpha = \hat{\mu}^\alpha, \quad \lambda^\alpha = \hat{\lambda}^\alpha, \\
\eta_\alpha &= \hat{\eta}_\alpha + f_\alpha, \quad \rho_\alpha \xi_\alpha = \rho_\alpha \hat{\xi}_\alpha + \rho_\alpha \frac{D^\alpha f_\alpha}{Dt} + \hat{m}_\alpha f_\alpha, \\
\psi_\alpha &= \hat{\psi}_\alpha - \theta_\alpha f_\alpha, \quad \epsilon_\alpha = \hat{\psi}_\alpha + \theta_\alpha \hat{\eta}_\alpha,
\end{aligned} \tag{3.16}$$

where f_α are arbitrary scalar functions of the variables (3.11), their space and time derivatives and functionals of their past histories. The partial stress tensors, the diffusive forces and couples, the entropy flux vectors (and hence the heat flux vectors) and the partial specific internal energies (3.14)₉ are unchanged and the energy equation (3.15) which imposes restrictions on the response functionals in (3.14) is also unchanged. If now (3.16)₁ to (3.16)₆ are substituted into (2.9)₁ and (3.5), we obtain the same differential equations for the variables (3.11) as those resulting from the set (3.14). Also the boundary conditions imposed on χ^α or T^α and on θ^α or p^α , together with appropriate initial conditions on χ^α and θ_α , are unaltered. Once the solutions for the deformations and temperatures have been determined, there remains some arbitrariness in $\eta_\alpha, \xi_\alpha, \psi_\alpha$ to the extent of the functionals f_α in (3.16), even though the differential equations and the boundary and the initial conditions do not involve f_α . An examination of the balance of entropy for the α th constituent as given by (3.5) reveals that f_α represents an internal generation of entropy which is accounted in (3.5) by an internal rate of production of entropy ξ_α . Moreover, this internal rate of production of entropy can be sustained in any part P_α without change in the partial specific internal energy ϵ_α and with no supply of entropy from external sources. This is a form of internal generation of entropy which seems to be physically unrealistic. In order to exclude this, we remove the arbitrariness in ξ_α by setting

$$\rho_\alpha \frac{D^\alpha f_\alpha}{Dt} + m_\alpha f_\alpha = 0, \quad \rho_\alpha f_\alpha \det F_\alpha = \rho_{\alpha 0} (X^\alpha) f_{\alpha 0} (X^\alpha), \tag{3.17}$$

where \underline{F}_α is the partial deformation gradient defined by $\underline{F}_\alpha = \partial \underline{x}^\alpha / \partial \underline{X}^\alpha$ and $f_{\alpha 0}$ is an arbitrary function of \underline{X}^α . Then, ξ_α is determined uniquely and η_α is only arbitrary to the extent of an additive function f_α given by (3.17). The function $f_{\alpha 0}(\underline{X}^\alpha)$, and hence f_α , is determined by specifying a value for η_α in some reference state.

The case in which all constituents are at a common temperature θ is of particular interest and may be regarded as a special case of the above theory in which all constituent temperatures are constrained to be equal, i.e.,

$$\theta_\alpha = \theta \quad (\alpha = 1, 2, \dots, v) \quad (3.18)$$

A constraint of this kind is possible only if $v-1$ of the external rates of supply of entropy are chosen so as to balance $v-1$ of the entropy equations (3.5) while the total external rate of supply of entropy

$$\rho s = \sum_{\alpha=1}^v \rho_\alpha s_\alpha \quad (3.19)$$

remains at our disposal. Equations (3.2) are then replaced by a single equation for the mixture as a whole in the form

$$\sum_{\alpha=1}^v \frac{d}{dt} \int_{P_\alpha} \rho_\alpha \eta_\alpha dv = \int_{P_\alpha} \rho (s + \xi) dv - \int_{\partial P_\alpha} k da \quad (3.20)$$

where

$$\rho \xi = \sum_{\alpha=1}^v \rho_\alpha \xi_\alpha, \quad k = \sum_{\alpha=1}^v k_\alpha = \underline{p} \cdot \underline{n}, \quad \underline{p} = \sum_{\alpha=1}^v \underline{p}^\alpha \quad (3.21)$$

and where the total heat flux and the total heat flux vector are given by

$$h = \underline{q} \cdot \underline{n}, \quad \underline{q} = \sum_{\alpha=1}^v \underline{q}^\alpha = \theta \underline{p} \quad (3.22)$$

The local field equation which follows from (3.20) reads as

$$\sum_{\alpha=1}^v \left(\rho_{\alpha} \frac{D^{\alpha} \eta_{\alpha}}{Dt} + m_{\alpha} \eta_{\alpha} \right) = \rho(s+\xi) - \operatorname{div} \underline{p} \quad (3.23)$$

and the energy equation (3.10) now becomes

$$\begin{aligned} & - \sum_{\alpha=1}^v \left[\rho_{\alpha} \left(\frac{D^{\alpha} \psi_{\alpha}}{Dt} + \eta_{\alpha} \frac{D^{\alpha} \theta}{Dt} \right) + m_{\alpha} \psi_{\alpha} \right] \\ & + \sum_{\alpha=1}^v \left[\underline{\mu}^{\alpha} \cdot \underline{v}^{\alpha} + \underline{T}^{\alpha} \cdot \operatorname{grad} \underline{v}^{\alpha} + \frac{1}{2} m_{\alpha} \underline{u}^{\alpha} \cdot \underline{u}^{\alpha} \right] \\ & - \rho \xi \theta - \underline{p} \cdot \operatorname{grad} \theta = 0 \quad . \end{aligned} \quad (3.24)$$

Before considering what restrictions arise from some form of second law of thermodynamics, we discuss in the next section a special case of the above thermo-mechanical theory for a mixture of inviscid fluids.

For later use, we need to record the expressions for the external mechanical work and the external heat supplied to the whole mixture occupying the region of space \mathcal{R} during the time interval $t_1 \leq t \leq t_2$. First, however, we observe that in the case of the mixture of inviscid fluids discussed in §4 the response functions for $\psi_{\alpha}, \eta_{\alpha}, \epsilon_{\alpha}$ depend only on the constituent densities ρ_{β} and the constituent temperatures θ_{β} but are independent of their rates, the velocities \underline{v}^{β} and the temperature gradients $\operatorname{grad} \theta_{\beta}$. An elastic mixture of this kind will be regarded as nondissipative in a sense that will be made precise later; and, in conjunction with an expression for the external mechanical work supplied to \mathcal{R} , will be used as a basis for establishing in §5 an inequality representing the second law of thermodynamics for dissipative materials. Keeping this background in mind, we assume that the constitutive response functions for $\epsilon_{\alpha}, \eta_{\alpha}$ include also dependence on the set of variables $\underline{v}^{\alpha}, \dot{\theta}_{\alpha}, \operatorname{grad} \theta_{\alpha}$ and their higher space and time derivatives and refer to this set collectively as \mathcal{V} . Further, let $\epsilon'_{\alpha}, \eta'_{\alpha}$ denote the respective values of $\epsilon_{\alpha}, \eta_{\alpha}$ when the set \mathcal{V} is put equal to zero in the response functions.*

Thus, for example,

* These definitions of $\epsilon'_{\alpha}, \eta'_{\alpha}$ do not exclude their dependence on the past histories.

$$\epsilon_\alpha = \epsilon_\alpha(\rho_\beta, \theta_\beta, v) \quad , \quad \epsilon'_\alpha = \epsilon'_\alpha(\rho_\beta, \theta_\beta) = \epsilon_\alpha(\rho_\beta, \theta_\beta, 0) \quad , \quad (3.25)$$

$$v = (\tilde{v}^\alpha, D^\alpha \theta_\alpha / Dt, \text{grad } \theta_\alpha, \dots) \quad ,$$

where the dots in (3.25)₃ refer to the higher space and time derivatives of $\tilde{v}^\alpha, D^\alpha \theta_\alpha / Dt, \text{grad } \theta_\alpha$. Then, with the help of (2.9) and the integral of (3.8) with respect to time, we obtain

$$\begin{aligned} W &= \int_{t_1}^{t_2} \left[\int_R \sum_{\alpha=1}^v \rho_\alpha \tilde{b}^\alpha \cdot \tilde{v}^\alpha dv + \int_{\partial R} \sum_{\alpha=1}^v \tilde{t}^\alpha \cdot \tilde{v}^\alpha da \right] dt \\ &= \sum_{\alpha=1}^v \int_R \left(\frac{1}{2} \rho_\alpha \tilde{v}^\alpha \cdot \tilde{v}^\alpha + \rho_\alpha \epsilon_\alpha \right) dv \Big|_{t_1}^{t_2} \\ &\quad + \int_{t_1}^{t_2} \int_R \left[- \sum_{\alpha=1}^v \theta_\alpha \left\{ \frac{\partial}{\partial t} (\rho_\alpha \eta'_\alpha) + \text{div}(\rho_\alpha \eta'_\alpha \tilde{v}^\alpha) \right\} + \sum_{\alpha=1}^v \rho_\alpha w_\alpha \right] dv dt \end{aligned} \quad (3.26)$$

and

$$\begin{aligned} H &= \int_{t_1}^{t_2} \left[\int_R \sum_{\alpha=1}^v \rho_\alpha \tilde{r}_\alpha dv - \int_{\partial R} \sum_{\alpha=1}^v h^\alpha da \right] dt \\ &= \int_{t_1}^{t_2} \int_R \left[\sum_{\alpha=1}^v \theta_\alpha \left\{ \frac{\partial (\rho_\alpha \eta'_\alpha)}{\partial t} + \text{div}(\rho_\alpha \eta'_\alpha \tilde{v}^\alpha) \right\} - \sum_{\alpha=1}^v \rho_\alpha w_\alpha \right] dv dt \quad , \end{aligned} \quad (3.27)$$

where

$$\begin{aligned} \psi'_\alpha &= \epsilon_\alpha - \theta_\alpha \eta'_\alpha \quad , \\ \rho_\alpha w_\alpha &= - \rho_\alpha \left(\frac{D^\alpha \epsilon_\alpha}{Dt} + \theta_\alpha \frac{D^\alpha \eta'_\alpha}{Dt} \right) - m_\alpha (\epsilon_\alpha - \theta_\alpha \eta'_\alpha) + \frac{1}{2} m_\alpha \tilde{u}^\alpha \cdot \tilde{u}^\alpha + \mu^\alpha \cdot \tilde{v}^\alpha + \tau^\alpha \cdot \text{grad } \tilde{v}^\alpha \quad , \\ \sum_{\alpha=1}^v \rho_\alpha w_\alpha &= - \sum_{\alpha=1}^v \theta_\alpha \left[\rho_\alpha \frac{D^\alpha (\eta_\alpha - \eta'_\alpha)}{Dt} + m_\alpha (\eta_\alpha - \eta'_\alpha) \right] \\ &\quad + \sum_{\alpha=1}^v (\rho_\alpha \xi_\alpha \theta_\alpha + \tilde{p}^\alpha \cdot \text{grad } \theta_\alpha) \quad . \end{aligned} \quad (3.28)$$

4. Mixture of inviscid fluids.

Consider a mixture of inviscid fluids with ν constituents. We define the properties of each constituent by the constitutive assumptions that the set of variables (3.12) are functions of

$$\rho_\beta, \theta_\beta, \text{grad } \rho_\beta, \text{grad } \theta_\beta \quad (\beta=1,2,\dots,\nu) \quad . \quad (4.1)$$

As indicated in §3 [following (3.13)], the equations (2.10), the conditions (2.13) and the energy equations (3.10) are regarded here as identities to be satisfied by all motions and all temperature distributions. Using this procedure and making use of (2.8), the application of standard techniques leads to

$$\psi'_\alpha = \psi_\alpha = \psi_\alpha(\rho_\beta, \theta_\beta) \quad , \quad m_\alpha = 0 \quad , \quad (4.2)$$

$$\rho_\alpha \eta'_\alpha = \rho_\alpha \eta_\alpha = - \sum_{\beta=1}^{\nu} \rho_\beta \frac{\partial \psi_\beta}{\partial \theta_\alpha} = - \rho \frac{\partial \psi}{\partial \theta_\alpha} \quad , \quad \rho \psi = \sum_{\alpha=1}^{\nu} \rho_\alpha \psi_\alpha \quad , \quad (4.3)$$

$$\tilde{T}^\alpha = - \tilde{I} \sum_{\beta=1}^{\nu} \rho_\alpha \rho_\beta \frac{\partial \psi_\beta}{\partial \rho_\alpha} \quad , \quad \tilde{\lambda}^\alpha = 0 \quad , \quad (4.4)$$

$$\begin{aligned} \tilde{\pi}^\alpha = & \sum_{\beta=1}^{\nu} \left(\rho_\alpha \frac{\partial \psi_\alpha}{\partial \rho_\beta} \text{grad } \rho_\beta - \rho_\beta \frac{\partial \psi_\beta}{\partial \rho_\alpha} \text{grad } \rho_\alpha \right) \\ & + \sum_{\beta=1}^{\nu} \left(\rho_\alpha \frac{\partial \psi_\alpha}{\partial \theta_\beta} \text{grad } \theta_\beta - \rho_\beta \frac{\partial \psi_\beta}{\partial \theta_\alpha} \text{grad } \theta_\alpha \right) \quad , \end{aligned} \quad (4.5)$$

$$\sum_{\alpha=1}^{\nu} \rho_\alpha w_\alpha = \sum_{\alpha=1}^{\nu} \left(\rho_\alpha \theta_\alpha \xi_\alpha + \tilde{\pi}^\alpha \cdot \text{grad } \theta_\alpha \right) = 0 \quad , \quad (4.6)$$

where \tilde{I} is the identity tensor and in writing (4.6) we have also recalled (3.28)₃.

In view of (4.6), we put

$$\rho_\alpha \theta_\alpha \xi_\alpha = - \tilde{\pi}^\alpha \cdot \text{grad } \theta_\alpha + \rho_\alpha \theta_\alpha \xi'_\alpha \quad , \quad \sum_{\alpha=1}^{\nu} \rho_\alpha \theta_\alpha \xi'_\alpha = 0 \quad . \quad (4.7)$$

Then, from (3.5) and (4.7) we have

$$\rho_\alpha r_\alpha + \rho_\alpha \theta_\alpha g'_\alpha - \operatorname{div} \underline{q}^\alpha = \rho_\alpha \theta_\alpha \frac{D^\alpha \eta_\alpha}{Dt} \quad , \quad \rho r - \operatorname{div} \underline{q} = \sum_{\alpha=1}^v \rho_\alpha \theta_\alpha \frac{D^\alpha \eta_\alpha}{Dt} \quad , \quad (4.8)$$

where the rate of supply of heat for the mixture and the total heat flux vector are defined by

$$\rho r = \sum_{\alpha=1}^v \rho_\alpha r_\alpha \quad , \quad \underline{q} = \sum_{\alpha=1}^v \underline{q}^\alpha \quad . \quad (4.9)$$

For a mixture of inviscid fluids characterized by (4.4) to (4.8), with the help of (4.8) and the results of §§2,3, we record below the expressions for the mixture as a whole representing (i) external work by body and surface forces on the mixture and (ii) external supply of energy to the mixture arising from the rate of supply of heat and the total surface flux of heat, both over a finite time interval $t_1 \leq t < t_2$:

$$\begin{aligned} W &= \int_{t_1}^{t_2} \left[\int_R \sum_{\alpha=1}^v \rho_\alpha \underline{b}^\alpha \cdot \underline{v}^\alpha \, dv + \int_{\partial R} \sum_{\alpha=1}^v \underline{t}^\alpha \cdot \underline{v}^\alpha \, da \right] dt \\ &= \sum_{\alpha=1}^v \int_R \left(\frac{1}{2} \rho_\alpha \underline{v}^\alpha \cdot \underline{v}^\alpha + \rho_\alpha \epsilon_\alpha \right) dv \Big|_{t_1}^{t_2} \\ &\quad - \int_{t_1}^{t_2} \int_R \sum_{\alpha=1}^v \theta_\alpha \left\{ \frac{\partial(\rho_\alpha \eta'_\alpha)}{\partial t} + \operatorname{div}(\rho_\alpha \eta'_\alpha \underline{v}^\alpha) \right\} dv \, dt \end{aligned} \quad (4.10)$$

and

$$\begin{aligned} H &= \int_{t_1}^{t_2} \left[\int_R \sum_{\alpha=1}^v \rho_\alpha r_\alpha \, dv - \int_{\partial R} \sum_{\alpha=1}^v h^\alpha \, da \right] dt \\ &= \int_{t_1}^{t_2} \int_R \sum_{\alpha=1}^v \theta_\alpha \left\{ \frac{\partial(\rho_\alpha \eta'_\alpha)}{\partial t} + \operatorname{div}(\rho_\alpha \eta'_\alpha \underline{v}^\alpha) \right\} dv \, dt \quad . \end{aligned} \quad (4.11)$$

In the above discussion of a mixture of inviscid fluids the response functions are assumed to depend only on the set of variables (4.1) which excludes the velocity vectors \underline{v}^α . An extension of the discussion to include dependence on the velocity vectors is carried out in §6. In the meantime, we observe that the development of the present section can be extended to include a mixture of elastic solids, or elastic solids and inviscid fluids. In general, the

constitutive assumption for a mixture of elastic materials requires that the variables (3.12) be functions of the temperature, temperature gradients, deformation gradients and second deformation gradients. With the help of (2.10), (2.13) and (3.10), it follows that the response functions for ψ_α, η_α depend only on the temperatures and deformation gradients. With these results and recalling the notations of §3, we may put $\psi'_\alpha = \psi_\alpha, \eta'_\alpha = \eta_\alpha$, and it can then be shown that the expressions for the external mechanical work \dot{W} and the external heat \dot{H} supplied to the mixture again reduce to the forms (4.10) and (4.11), respectively. We make use of these results in §5.

In the case in which all constituent temperatures are equal, instead of (3.10), the energy equation is given by (3.24) and the results (4.2) to (4.6) are replaced by

$$\psi_\alpha = \psi_\alpha(\rho_\beta, \theta), \quad m_\alpha = 0, \quad (4.12)$$

$$\sum_{\alpha=1}^v \rho_\alpha \eta_\alpha = - \sum_{\beta=1}^v \rho_\beta \frac{\partial \psi_\beta}{\partial \theta}, \quad (4.13)$$

or

$$\eta = - \frac{\partial \psi}{\partial \theta}, \quad \rho \eta = \sum_{\alpha=1}^v \rho_\alpha \eta_\alpha, \quad \rho \psi = \sum_{\alpha=1}^v \rho_\alpha \psi_\alpha, \quad (4.13a)$$

$$\tilde{T}^\alpha = - \tilde{I} \sum_{\beta=1}^v \rho_\alpha \rho_\beta \frac{\partial \psi_\beta}{\partial \rho_\alpha}, \quad \tilde{\lambda}^\alpha = 0, \quad (4.14)$$

$$\mu^\alpha = \sum_{\beta=1}^v \left(\rho_\alpha \frac{\partial \psi_\alpha}{\partial \rho_\beta} \text{grad } \rho_\beta - \rho_\beta \frac{\partial \psi_\beta}{\partial \rho_\alpha} \text{grad } \rho_\alpha \right) + \rho_\alpha \left(\frac{\partial \psi_\alpha}{\partial \theta} + \eta_\alpha \right) \text{grad } \theta, \quad (4.15)$$

$$\rho \xi \theta + \tilde{p} \cdot \text{grad } \theta = 0. \quad (4.16)$$

Also, instead of (4.8)₂, we now have

$$\text{pr-div } \tilde{q} = \theta \sum_{\alpha=1}^v \rho_\alpha \frac{D^\alpha \eta_\alpha}{Dt}. \quad (4.17)$$

For a mixture with many constituent temperatures, Craine, Green and Naghdi (2) have discussed more general constitutive equations than is implied by the dependence of (3.12) on the variables (4.1). The detailed development of their work on a mixture of viscous elastic materials is such that direct comparison of their results with (4.2) to (4.5) is difficult. However, if the energy equation (3.10) is not regarded as an identity and the entropy inequality employed by Craine et al. (2) is used to impose restrictions on the forms of $\tilde{T}^\alpha, \psi_\alpha, \eta_\alpha, \mu^\alpha, \lambda^\alpha$ as functions of the variables (4.1), then the following results emerge:

$$\psi_\alpha = \psi_\alpha(\rho_\beta, \theta_\beta) \quad , \quad m_\alpha = 0 \quad , \quad (4.18)$$

$$\rho_\alpha \eta_\alpha = - \theta_\alpha \sum_{\beta=1}^v \frac{\rho_\beta}{\theta_\beta} \frac{\partial \psi_\beta}{\partial \theta_\alpha} \quad , \quad (4.19)$$

$$\tilde{T}^\alpha = - \tilde{T}^\alpha_\alpha \sum_{\beta=1}^v \frac{\rho_\alpha \rho_\beta}{\theta_\beta} \frac{\partial \psi_\beta}{\partial \rho_\alpha} \quad , \quad \lambda^\alpha = 0 \quad , \quad (4.20)$$

$$\begin{aligned} \tilde{\mu}^\alpha = & \theta_\alpha \sum_{\beta=1}^v \left(\frac{\rho_\alpha}{\theta_\alpha} \frac{\partial \psi_\alpha}{\partial \rho_\beta} \text{grad } \rho_\beta - \frac{\rho_\beta}{\theta_\beta} \frac{\partial \psi_\beta}{\partial \rho_\alpha} \text{grad } \rho_\alpha \right) \\ & + \theta_\alpha \sum_{\beta=1}^v \left(\frac{\rho_\alpha}{\theta_\alpha} \frac{\partial \psi_\alpha}{\partial \theta_\beta} \text{grad } \theta_\beta - \frac{\rho_\beta}{\theta_\beta} \frac{\partial \psi_\beta}{\partial \theta_\alpha} \text{grad } \theta_\alpha \right) \quad (\alpha=1, \dots, v-1) \quad , \end{aligned} \quad (4.21)$$

$$\tilde{\mu}^v = - \sum_{\alpha=1}^v \tilde{\mu}^\alpha \quad . \quad (4.22)$$

The above results differ from those given by (4.2) to (4.5), although the differences disappear when all the temperatures are equal. It should be emphasized that the formulae (4.2) to (4.5) have been obtained without any appeal to a second law of thermodynamics, in contrast to the results (4.18) to (4.22), which are obtained here in the spirit of earlier procedures with the use of an entropy inequality.

5. The second law of thermodynamics. Restrictions on heat conduction vectors and internal energies.

Previously [see Green and Naghdi (9), §4], we examined the nature of thermodynamic irreversibility arising from a mathematical interpretation of a statement of the second law of thermodynamics, namely that "it is impossible completely to reverse a process in which energy is transformed into heat by friction." This led us to postulate an inequality which is different from the Clausius-Duhem inequality; some of the undesirable features of the latter inequality are discussed in §7 of Green and Naghdi (9).

Here we follow a procedure for mixtures which is similar to that used previously for single phase continua. First, we observe that the expressions $(3.26)_1$, when evaluated for a given process, may be either positive or negative depending on whether the external work is supplied to, or is withdrawn from, \mathcal{R} . This external work is also represented by $(3.26)_2$ in terms of both thermal and mechanical variables but not every term in $(3.26)_2$ need necessarily be positive (zero or negative), even though the external work may be positive (zero or negative). Thus, following a discussion similar to that in (2,10), with reference to a dissipative mixture we assume that in every admissible process a part of the external work done is always nonnegative. Then, in a process and its reverse process at the end of which the mixture has returned to its same state, some of the work done is always transformed into heat. Hence, we write

$$w = w_1 + w_2, \quad w_2 \geq 0.$$

The above also implies that

$$w \geq w_1$$

and w is bounded below, the bound depending on the process.

In order to identify the two parts w_1 and w_2 , we note from (4.6) and (3.26) that in the case of a mixture of inviscid fluids or elastic materials discussed in §4 the expression for the external mechanical work supplied to R reduces to (4.10)[†]. We now regard an elastic mixture of this kind as nondissipative in the sense that no restriction is placed on the external mechanical work supplied to R and identify w_1 with the right-hand side of (3.26)₂ after setting $\sum_{\alpha=1}^v \rho_{\alpha} w_{\alpha} = 0$. Keeping this in mind, we rewrite the last inequality as

$$w \leq \sum_{\alpha=1}^v \int_R \rho_{\alpha} \left(\frac{1}{2} \tilde{v}^{\alpha} \cdot \tilde{v}^{\alpha} + \epsilon_{\alpha} \right) dv \Big|_{t_1}^{t_2} - \int_{t_1}^{t_2} \int_R \sum_{\alpha=1}^v \theta_{\alpha} \left[\frac{\partial(\rho_{\alpha} \eta'_{\alpha})}{\partial t} + \operatorname{div}(\rho_{\alpha} \eta'_{\alpha} \tilde{v}^{\alpha}) \right] dv dt \quad (5.1)$$

and assume that (5.1) holds for every thermo-mechanical process. The combination of (3.26)₂ and the assumption (5.1) yields

$$\int_{t_1}^{t_2} \int_R \sum_{\alpha=1}^v \rho_{\alpha} w_{\alpha} dv dt \geq 0 \quad (5.2)$$

for all times t_1, t_2 ($t_1 \leq t_2$). Since t_1, t_2 are arbitrary and $\sum_{\alpha=1}^v \rho_{\alpha} w_{\alpha}$ has already been assumed to be continuous, it follows that

$$\sum_{\alpha=1}^v \int_R \rho_{\alpha} w_{\alpha} dv \geq 0 \quad (5.3)$$

for all thermo-mechanical processes. With the help of (3.27) and (5.3), we also have

$$w \leq \sum_{\alpha=1}^v \int_{t_1}^{t_2} \int_R \sum_{\alpha=1}^v \theta_{\alpha} \left[\frac{\partial(\rho_{\alpha} \eta'_{\alpha})}{\partial t} + \operatorname{div}(\rho_{\alpha} \eta'_{\alpha} \tilde{v}^{\alpha}) \right] dv dt \quad (5.4)$$

so that the external heat supplied to the whole mixture is bounded above in every process. Alternatively, some of the heat supplied to the mixture in every process is always nonpositive.

[†]It may be recalled that the expressions (4.10) and (4.11) hold also for a mixture of elastic solids (or fluid-solid) in which dependence on the velocity vectors is excluded, as was noted in the paragraph following (4.11).

The development of this section began with an examination of the expression for the supply of external mechanical work to the whole mixture occupying the region R at time t and this led us to postulate the inequality (5.1) from which the thermodynamic condition (5.3) was deduced. It is also possible to obtain a similar condition for every part of the mixture. For the latter, instead of considering the total mechanical work during a given time interval, we consider the rate at which mechanical work is supplied to a part of the mixture. Thus, with reference to the present configuration and for material volumes which coincide at time t and occupy parts $P_\alpha = P$ of R , the rate $W(t)$ at which external work is supplied to a part P of the mixture is

$$W(t) = \sum_{\alpha=1}^v \int_P \rho_\alpha b_\alpha^\alpha \cdot \tilde{v}^\alpha dv + \sum_{\alpha=1}^v \int_{\partial P_\alpha} t_\alpha^\alpha \cdot \tilde{v}_i^\alpha da \quad (5.5)$$

Using results similar to (3.26) and (3.28) but with R replaced with P and the limit of integration t_2 replaced with t , the last expression can be put in the form

$$W(t) = \sum_{\alpha=1}^v \frac{d}{dt} \int_P \left(\frac{1}{2} \rho_\alpha \tilde{v}^\alpha \cdot \tilde{v}^\alpha + \rho_\alpha \epsilon_\alpha \right) dv + \sum_{\alpha=1}^v \int_P \left\{ -\theta_\alpha \left[\frac{\partial(\rho_\alpha \eta_\alpha')}{\partial t} + \text{div}(\rho_\alpha \eta_\alpha' \tilde{v}^\alpha) \right] + \rho_\alpha w_\alpha \right\} dv \quad (5.6)$$

By an argument similar to that which led to (5.1), for each part P of the mixture we write

$$W(t) \geq \sum_{\alpha=1}^v \frac{d}{dt} \int_P \left(\frac{1}{2} \rho_\alpha \tilde{v}^\alpha \cdot \tilde{v}^\alpha + \rho_\alpha \epsilon_\alpha \right) dv - \sum_{\alpha=1}^v \int_P \theta_\alpha \left[\frac{\partial(\rho_\alpha \eta_\alpha')}{\partial t} + \text{div}(\rho_\alpha \eta_\alpha' \tilde{v}^\alpha) \right] dv \quad (5.7)$$

and assume that (5.7) holds for every thermo-mechanical process. The combination of (5.6) and the assumption (5.7) yields

$$\int_P \sum_{\alpha=1}^v \rho_\alpha w_\alpha dv \geq 0 \quad (5.8)$$

for every part P . From this last inequality follows the local form

$$\sum_{\alpha=1}^v \rho_{\alpha} w_{\alpha} \geq 0, \quad (5.9)$$

which must hold for all thermo-mechanical processes.

We supplement the above interpretation of the second law with two further inequalities which stem from the statement that "heat cannot pass spontaneously from a body of lower temperature to a body of higher temperature." To this end, we consider first the heat flux response in equilibrium cases for which the heat flow is steady. By equilibrium we mean that

$$\dot{\gamma}^{\alpha} = 0, \quad \tilde{F}^{\alpha} = \tilde{F}_{\infty}^{\alpha}, \quad \theta^{\alpha} = \theta, \quad \rho_{\alpha} = \rho_{\alpha 0} \text{ for all } t, \quad (5.10)$$

where \tilde{F}^{α} is the deformation gradient for the constituent C_{α} , the tensor $\tilde{F}_{\infty}^{\alpha}$, the common temperature θ and the densities $\rho_{\alpha 0}$, as well as all other relevant functions, are independent of t but may depend on x . Then, $m_{\alpha} = 0$ and the conservation equations (3.5) and (3.8) become

$$\rho_{\alpha} (s_{\alpha} + \xi_{\alpha}) = \operatorname{div} \tilde{p}^{\alpha}, \quad \sum_{\alpha=1}^v (\rho_{\alpha} \xi_{\alpha} \theta + \tilde{p}^{\alpha} \cdot \operatorname{grad} \theta) = 0. \quad (5.11)$$

Also, since

$$\begin{aligned} pr &= \sum_{\alpha=1}^v \rho_{\alpha} r_{\alpha} = \sum_{\alpha=1}^v \rho_{\alpha} \theta s_{\alpha} = \theta \sum_{\alpha=1}^v \rho_{\alpha} s_{\alpha}, \\ q &= \sum_{\alpha=1}^v q^{\alpha} = \sum_{\alpha=1}^v \theta \tilde{p}^{\alpha} = \theta \sum_{\alpha=1}^v \tilde{p}^{\alpha}, \end{aligned} \quad (5.12)$$

it follows from (5.11) that

$$pr = \operatorname{div} q. \quad (5.13)$$

The equation (5.13), which is obtained here for a mixture in equilibrium, has the same form as the corresponding result for a single phase continuum; and thus, for equilibrium cases under discussion, we again adopt the classical heat conduction inequality

$$-\underline{q} \cdot \text{grad } \theta \geq 0 \quad (5.14)$$

for all time-independent temperature fields (5.10)₃. We note that the inequality (5.14) can be written in the alternative form

$$-\sum_{\alpha=1}^v \underline{p}^{\alpha} \cdot \text{grad } \theta \geq 0, \quad (5.15)$$

in view of (5.12) and since $\theta > 0$.

In the remainder of this section, we suppose that the mixture is at rest with $\underline{v}^{\alpha} = 0$ for all time and with the densities ρ_{α} and with the deformation gradients $\partial \underline{x}^{\alpha} / \partial \underline{x}^{\alpha}$ everywhere constant for all time. Then $m_{\alpha} = 0$ and the total mass density $\rho = \sum_{\alpha=1}^v \rho_{\alpha}$, which is positive, is constant. In addition, we restrict the temperature fields to be spatially homogeneous and equal so that $\theta_{\alpha} = \theta(t)$. The specific internal energies ϵ_{α} which will depend on ρ_{α} , $\partial \underline{x}^{\alpha} / \partial \underline{x}^{\alpha}$, θ and its history will be functions of t , independent of \underline{x} . Moreover, recalling (4.9), from combination of (3.5) and (3.8) we have

$$\text{pr-div } \underline{q} = \frac{\partial}{\partial t} (\rho \epsilon), \quad \rho \epsilon = \sum_{\alpha=1}^v \rho_{\alpha} \epsilon_{\alpha}, \quad (5.16)$$

where ϵ is a function of t independent of \underline{x} . Since $\underline{v}^{\alpha} = 0$ everywhere, no mechanical work is supplied to the whole mixture occupying the region \mathcal{R} at time t . Then, by integration of (5.16)₁ with respect to t , the heat supplied to \mathcal{R} during the time interval $t_1 \leq t \leq t_2$ is

$$\mathcal{H} = \int_{\mathcal{R}} \rho \epsilon \, dv \Big|_{t_1}^{t_2} = [\epsilon]_{t_1}^{t_2} \int_{\mathcal{R}} \rho \, dv. \quad (5.17)$$

We now suppose that the mixture has been in thermal equilibrium during some interval of time up to the time t_1 with constant temperature θ_1 and constant internal energy $\bar{\epsilon}$. We then assume that whenever heat is supplied to the mixture according to (5.17), the temperature $\theta(t)$ throughout \mathcal{R} will be increased. Hence, we impose the condition that

$$[\theta]_{t_1}^{t_2} > 0 \text{ whenever } \mathcal{H} > 0 . \quad (5.18)$$

Since ρ is positive, it follows from (5.17) and (5.18) that

$$\theta(t) - \theta_1 > 0 \text{ whenever } \epsilon(t) - \bar{\epsilon} > 0 \quad (5.19)$$

for all times $t > t_1$.

6. Further discussion of inviscid fluids.

In order to illustrate the nature of the preceding thermodynamical developments, we return to a mixture of inviscid fluids which is partially discussed in §4. For simplicity, however, we limit attention to a mixture of two fluid constituents whose masses are separately conserved. Thus, we write

$$m_1 = \frac{D^1 \rho_1}{Dt} + \rho_1 \operatorname{div} \underline{v}^1 = 0, \quad m_2 = \frac{D^2 \rho_2}{Dt} + \rho_2 \operatorname{div} \underline{v}^2 = 0 \quad (6.1)$$

and, in view of (2.13)_{2,3}, we adopt the notations

$$\underline{\mu}^1 = -\underline{\mu}^2 = \underline{\mu}, \quad \underline{\lambda}^1 = -\underline{\lambda}^2 = -\underline{\lambda}. \quad (6.2)$$

Constitutive equations for such fluids usually include the dependence on the velocity vectors but these were omitted in the discussion of section 4. We now assume that the set of variables

$$\underline{T}^1, \underline{T}^2, \psi_1, \psi_2, \eta_1, \eta_2, \xi_1, \xi_2, \underline{\mu}, \underline{\lambda}, \underline{p}^1, \underline{p}^2 \quad (6.3)$$

are functions of

$$\rho_1, \rho_2, \operatorname{grad} \rho_1, \operatorname{grad} \rho_2, \theta_1, \theta_2, \operatorname{grad} \theta_1, \operatorname{grad} \theta_2 \quad (6.4)$$

and $\underline{v}^1, \underline{v}^2$. In view of invariance conditions under superposed rigid body motions, however, the variables $\underline{v}^1, \underline{v}^2$ must be replaced by

$$\underline{v}^1 - \underline{v}^2 = \underline{a}. \quad (6.5)$$

In accordance with the procedure of §3, since (2.10), (2.13) and the energy equation (3.10) must be satisfied as identities for all motions and all temperature distributions, we then obtain

$$\begin{aligned}\psi_1 &= \hat{\psi}_1(\rho_1, \rho_2, \theta_1, \theta_2, \underline{a}) , \quad \psi_2 = \hat{\psi}_2(\rho_1, \rho_2, \theta_1, \theta_2, \underline{a}) , \\ \rho \psi &= \rho_1 \psi_1 + \rho_2 \psi_2 , \quad \psi = \hat{\psi}(\rho_1, \rho_2, \theta_1, \theta_2) , \\ \rho_1 \eta_1 &= - \rho \frac{\partial \hat{\psi}}{\partial \theta_1} , \quad \rho_2 \eta_2 = - \rho \frac{\partial \hat{\psi}}{\partial \theta_2} ,\end{aligned}\tag{6.6}$$

$$\begin{aligned}\tilde{\pi}^1 &= - (\rho_1^2 \frac{\partial \hat{\psi}_1}{\partial \rho_1} + \rho_1 \rho_2 \frac{\partial \hat{\psi}_2}{\partial \rho_1}) \tilde{I} + \rho_1 \frac{\partial \hat{\psi}_1}{\partial \underline{a}} \tilde{a} , \\ \tilde{\pi}^2 &= - (\rho_1 \rho_2 \frac{\partial \hat{\psi}_1}{\partial \rho_2} + \rho_2^2 \frac{\partial \hat{\psi}_2}{\partial \rho_2}) \tilde{I} - \rho_1 \frac{\partial \hat{\psi}_1}{\partial \underline{a}} \tilde{a} ,\end{aligned}\tag{6.7}$$

$$\begin{aligned}\bar{\mu} &= \tilde{\pi} + \rho_1 \frac{\partial \psi_1}{\partial \rho_2} \text{grad } \rho_2 - \rho_2 \frac{\partial \psi_2}{\partial \rho_1} \text{grad } \rho_1 \\ &\quad + \rho_1 \frac{\partial \psi_1}{\partial \theta_2} \text{grad } \theta_2 - \rho_2 \frac{\partial \psi_2}{\partial \theta_1} \text{grad } \theta_1 ,\end{aligned}\tag{6.8}$$

$$\rho_1 \xi_1 \theta_1 + \rho_2 \xi_2 \theta_2 + \tilde{\pi}^1 \cdot \text{grad } \theta_1 + \tilde{\pi}^2 \cdot \text{grad } \theta_2 - \bar{\mu} \cdot \underline{a} = 0 ,\tag{6.9}$$

where $\bar{\mu}$ is a function of the variables (6.4) and (6.5). Apart from invariance considerations no further reduction in the form of these results is possible without the use of the thermodynamic restrictions (5.3) or (5.9) and (5.15) or without employing more restrictive constitutive assumptions. Here we use the inequality (5.9) with w_α given by (3.28). From this inequality, we may deduce the result

$$\bar{\mu} \cdot \underline{a} \geq 0\tag{6.10}$$

for all thermo-mechanical processes. Now put

$$\bar{\mu} = \bar{\mu}' + \bar{\mu}'' ,$$

where $\bar{\mu}'$ is the part of the response function for $\bar{\mu}$ when \underline{a} is set equal to zero. Then, assuming that $\bar{\mu}$ is a continuous function of its arguments, from (6.10) we deduce the results

$$\bar{r}^{\perp} = 0 \quad , \quad \bar{r}^{\perp} \cdot a \neq 0 \quad . \quad (6.11)$$

Also some restrictions on the forms of the response functions \hat{p}_1, \hat{p}_2 may be found with the help of (5.15), but we leave the discussion at this point.

7. Flow of a fluid through a rigid solid.

In many problems involving the flow of a fluid through a porous solid, the latter is often regarded as a rigid, rather than deformable, solid; and, in addition, both media are assumed to be at the same temperature. Our main interest here is to explore a further application of the theory of earlier sections with reference to the flow of a homogeneous incompressible viscous fluid through a porous solid when the fluid and the solid are at different constituent temperatures; and, in order to avoid undue complications, we consider the solid to be stationary, homogeneous and rigid.

Let the incompressible viscous fluid, with its mass element conserved, be referred to as the constituent v_1 and let the stationary, homogeneous and rigid solid be identified as the constituent v_2 . Then, ρ_1 and ρ_2 are constants,

$$m_1 = 0, \quad m_2 = 0, \quad \operatorname{div} \underline{v}^1 = 0, \quad \underline{v}^2 = 0 \quad (7.1)$$

and by (2.13)_{2,3,4} we also have

$$\underline{\mu}^2 = -\underline{\mu}^1, \quad \underline{\lambda}^2 = -\underline{\lambda}^1, \quad \underline{\tau}^2 = -\underline{\tau}^1. \quad (7.2)$$

The energy equation (3.10) in this case becomes

$$\begin{aligned} & -\rho_1 \left(\frac{D^1 \psi_1}{Dt} + \eta_1 \frac{D^1 \theta_1}{Dt} \right) - \rho_2 \left(\frac{\partial \psi_2}{\partial t} + \eta_2 \frac{\partial \theta_2}{\partial t} \right) \\ & + \underline{\mu}^1 \cdot \underline{v}^1 + \underline{\tau}^1 \cdot \operatorname{grad} \underline{v}^1 - \rho_1 \xi_1 \theta_1 - \rho_2 \xi_2 \theta_2 \\ & - \underline{p}^1 \cdot \operatorname{grad} \theta_1 - \underline{p}^2 \cdot \operatorname{grad} \theta_2 = 0. \end{aligned} \quad (7.3)$$

Because of the incompressibility condition (7.1)₃, the stress tensor \underline{T}^1 is undetermined to the extent of an additive hydrostatic pressure \bar{p} so that

$$\underline{T}^1 = -\bar{p} \underline{I} + \bar{\underline{T}}, \quad (7.4)$$

where \bar{p} is an arbitrary scalar function of \underline{x}, t and \bar{T} is to be specified by a constitutive equation.

For the two constituents under consideration, we introduce the constitutive assumptions that

$$\bar{T}, \bar{\mu}^1, \bar{\lambda}^1, \bar{p}^1, \bar{p}^2, \psi_1, \psi_2, \eta_1, \eta_2, \xi_1, \xi_2 \quad (7.5)$$

are functions of the set of variables

$$\theta_1, \theta_2, \text{grad } \theta_1, \text{grad } \theta_2, \underline{v}, \text{grad } \underline{v} \quad (\underline{v}^1 = \underline{v}) \quad (7.6)$$

In the absence of the stationary rigid solid, invariance requirements under superposed rigid body motions would indicate that the velocity \underline{v} and the skew part of $\text{grad } \underline{v}$ should be excluded from the list of variables (7.6). However, in the present study in which the fluid flows through a stationary rigid solid no reduction in the variables (7.6) is possible.

According to the procedure outlined in §3, the energy equation (7.3) is to be regarded as an identity for all motions and all temperature fields. Hence, with the use of (7.4) and the above constitutive assumptions, application of standard techniques results in

$$\begin{aligned} \hat{\psi}_1 &= \hat{\psi}_1'(\theta_1, \theta_2) + \hat{\psi}_1''(\theta_1, \theta_2, \underline{v}) \quad , \quad \hat{\psi}_1'''(\theta_1, \theta_2, \underline{v}) = 0 \quad , \\ \hat{\psi}_2 &= \hat{\psi}_2'(\theta_1, \theta_2) + \hat{\psi}_2''(\theta_1, \theta_2, \underline{v}) \quad , \quad \hat{\psi}_2'''(\theta_1, \theta_2, \underline{v}) = 0 \quad , \\ \psi &= \hat{\psi}(\theta_1, \theta_2) \quad , \quad \rho\psi = \rho\psi_1' + \rho_2\psi_2' \quad , \quad \rho_1\psi_1'' + \rho_2\psi_2'' = 0 \quad , \end{aligned} \quad (7.7)$$

$$\rho_1\eta_1 = -\rho \frac{\partial \hat{\psi}}{\partial \theta_1} \quad , \quad \rho_2\eta_2 = -\rho \frac{\partial \hat{\psi}}{\partial \theta_2} \quad (7.8)$$

Hence, η_1 and η_2 depend only on the constituent temperatures θ_1, θ_2 and coincide respectively with η_1' and η_2' in the notation of §3. Also, with the help of (7.7) and (7.8) the identity (7.3) reduces to

$$\begin{aligned}
& (\bar{\mu}^1 - \rho_1 \frac{\partial \hat{\psi}_1}{\partial \theta_2} \text{grad } \theta_2 + \rho_2 \frac{\partial \hat{\psi}_2}{\partial \theta_1} \text{grad } \theta_1) \cdot \underline{v} \\
& + (\bar{T} - \rho_1 \frac{\partial \hat{\psi}_1}{\partial v} v) \cdot \text{grad } v - \rho_1 \xi_1 \theta_1 - \rho_2 \xi_2 \theta_2 \\
& - \bar{p}^1 \cdot \text{grad } \theta_1 - \bar{p}^2 \cdot \text{grad } \theta_2 = 0 .
\end{aligned} \tag{7.9}$$

Next, we turn to the inequality (5.9) with w_α given by (3.28)₂ and obtain

$$\begin{aligned}
\bar{\mu}^1 &= \rho_1 \frac{\partial \hat{\psi}_1}{\partial \theta_2} \text{grad } \theta_2 - \rho_2 \frac{\partial \hat{\psi}_2}{\partial \theta_1} \text{grad } \theta_1 + \bar{\mu} , \\
\bar{\mu} \cdot \underline{v} + (\bar{T} - \rho_1 \frac{\partial \hat{\psi}_1}{\partial v} v) \text{grad } v &\geq 0 ,
\end{aligned} \tag{7.10}$$

where $\bar{\mu}$ and \bar{T} are functions of the variables (7.6) which vanish when \underline{v} and $\text{grad } v$ are both zero.

In the rest of this section, we limit the discussion to a linearized theory about an equilibrium state in which $\underline{v} = \underline{0}$ and $\theta_1 = \theta_2 = \bar{\theta}$, $\bar{\theta}$ being a constant. We also assume that the rigid solid is homogeneous and isotropic with a center of symmetry. Thus, we set

$$\theta_1 = \bar{\theta}(1 + \alpha + \beta) , \quad \theta_2 = \bar{\theta}(1 + \alpha) \tag{7.11}$$

and retain only linear terms in α, β, v in all constitutive equations for $\bar{\mu}^1, \bar{T}, \bar{p}^1, \bar{p}^2, \eta_1, \eta_2$. However, in view of the relations (7.8) and the energy identity (7.9), for consistency we retain both the linear and the quadratic terms in α, β, v in the expressions for $\psi_1, \psi_2, \psi, \xi_1, \xi_2$. Thus, making use of (7.7) and remembering that the rigid solid is assumed to be homogeneous and isotropic, we write

$$\begin{aligned}
\frac{\rho_1 \hat{\psi}_1}{\bar{\theta}} &= v_0 - \gamma_1 \alpha - \gamma_2 \beta - \frac{1}{2} \gamma_3 \alpha^2 - \gamma_4 \alpha \beta - \frac{1}{2} \gamma_5 \beta^2 + \gamma v \cdot v , \\
\frac{\rho_2 \hat{\psi}_2}{\bar{\theta}} &= \bar{v}_0 - \bar{\gamma}_1 \alpha - \bar{\gamma}_2 \beta - \frac{1}{2} \bar{\gamma}_3 \alpha^2 - \bar{\gamma}_4 \alpha \beta - \frac{1}{2} \bar{\gamma}_5 \beta^2 - \gamma v \cdot v , \\
\frac{\rho \hat{\psi}}{\bar{\theta}} &= \delta_0 - \delta_1 \alpha - \delta_2 \beta - \frac{1}{2} \delta_3 \alpha^2 - \delta_4 \alpha \beta - \frac{1}{2} \delta_5 \beta^2 ,
\end{aligned} \tag{7.12}$$

where the coefficients $\delta_0, \dots, \delta_5$ are related to $\bar{v}_0, \dots, \bar{\gamma}_5$ through (7.7)₇.

In addition

$$\begin{aligned}\bar{p}^1 &= D_1 v + D_2 \text{grad } \alpha + D_3 \text{grad } \beta, \\ \bar{p}^1 &= D_4 v - D_5 \text{grad } \alpha - D_6 \text{grad } \beta, \\ \bar{p}^2 &= D_7 v = D_8 \text{grad } \alpha - D_9 \text{grad } \beta,\end{aligned}\tag{7.13}$$

and

$$\begin{aligned}\bar{T} &= (\mu + \mu_1) \text{grad } v + (\mu - \mu_1) (\text{grad } v)^T, \\ \rho_1 \xi_1 &= -D_{10} \alpha - D_{11} \beta + \rho_1 \bar{\xi}_1, \\ \rho_2 \xi_2 &= D_{10} \alpha + D_{11} \beta + \rho_2 \bar{\xi}_2,\end{aligned}\tag{7.14}$$

where $v_0, \dots, \delta_5, D_1, \dots, D_{11}, \mu, \mu_1$ are constants while $\bar{\xi}_1, \bar{\xi}_2$ are quadratic functions in the variables

$$\alpha, \beta, \text{grad } \alpha, \text{grad } \beta, v, \text{grad } v\tag{7.15}$$

and the partial internal production of entropies ξ_1, ξ_2 both vanish in the equilibrium state. In $(7.14)_{2,3}$ the linear parts of ξ_1, ξ_2 have been chosen so that the identity (1.9) is satisfied and the restrictions on the forms of $\bar{\xi}_1$ or $\bar{\xi}_2$ arise through the quadratic terms in (7.9). Also, by (7.8), (7.11) and (7.12), the expressions for the partial specific entropies are

$$\begin{aligned}\rho_1 \eta_1 &= -\frac{\rho}{\theta} \frac{\partial \hat{\psi}}{\partial \beta} = \delta_2 + \delta_4 \alpha + \delta_5 \beta, \\ \rho_2 \eta_2 &= -\frac{\rho}{\theta} \left(\frac{\partial \hat{\psi}}{\partial \alpha} - \frac{\partial \hat{\psi}}{\partial \beta} \right) = \delta_1 - \delta_2 + (\delta_3 - \delta_4) \alpha + (\delta_4 - \delta_5) \beta.\end{aligned}\tag{7.16}$$

With the help of $(7.13)_1$ and $(7.14)_1$, the inequality $(7.10)_2$ which holds for all processes may be used to show that

$$D_2 = 0, \quad D_3 = 0, \quad D_1 \geq 0, \quad \mu \geq 0, \quad \mu_1 \geq 0.\tag{7.17}$$

Our second thermodynamic condition (5.15), which holds in equilibrium with $\theta_1 = \theta_2$, reduces in the present problem to

$$-(p^1 + p^2) \cdot \text{grad } \alpha > 0 \quad \text{when } \beta = 0, \underline{v} = 0. \quad (7.18)$$

After substitution from (7.13), we readily obtain the condition

$$D_5 + D_8 \geq 0. \quad (7.19)$$

Further, when $\theta_1 = \theta_2$ or $\beta = 0$, the value of $p\epsilon = \rho_1 \epsilon_1 + \rho_2 \epsilon_2$ is $\delta_0 + \delta_1 + \delta_3 \alpha$ as far as the terms linear in α are concerned. Then, the third thermodynamic condition (5.19) requires that

$$\delta_3 \geq 0. \quad (7.20)$$

Making use of (7.1), (7.13)_{2,3}, (7.14) and (7.16) and retaining only the linear terms, the entropy balance equations become

$$\begin{aligned} \delta_4 \frac{\partial \alpha}{\partial t} + \delta_5 \frac{\partial \beta}{\partial t} &= \rho_1 s_1 - D_{10} \alpha - D_{11} \beta + D_5 \nabla^2 \alpha + D_6 \nabla^2 \beta, \\ (\delta_3 - \delta_4) \frac{\partial \alpha}{\partial t} + (\delta_4 - \delta_5) \frac{\partial \beta}{\partial t} &= \rho_2 s_2 + D_{10} \alpha + D_{11} \beta + D_8 \nabla^2 \alpha + D_9 \nabla^2 \beta, \end{aligned} \quad (7.21)$$

where ∇^2 stands for the Laplacian operator. The above differential equations, which serve to determine the temperatures α and β , are independent of the velocity \underline{v} . For the present discussion, we do not record the differential equation resulting from the balance of momentum which is an equation for \underline{v} and p ; the remaining equation involving \underline{v} is, of course, the incompressibility condition (7.1)₃.

Returning to (7.21), we note that so far we have only obtained the thermodynamic restrictions (7.19) and (7.20) on the constant coefficients which occur in the entropy balance equations. Our previous procedure of using an entropy inequality

of the Clausius-Duhem type [see the inequality (9.5) in the paper of Craine, Green and Naghdi (2)] would yield further restrictions on the coefficients $D_5, D_6, D_8, D_9, D_{10}, D_{11}$, but not on $\delta_3, \delta_4, \delta_5$; nevertheless, we do not adopt this approach here.

In closing this section, we indicate what further restrictions may be imposed on the coefficients $\delta_3, \dots, \delta_{11}$ in order to render, under suitable boundary and initial conditions, the solutions of (7.21) unique. We suppose that the stationary rigid solid always occupies a region of space \mathcal{R} and that the fluid also occupies the same region so that

$$\underline{v} \cdot \underline{n} = 0 \quad \text{on } \partial\mathcal{R} . \quad (7.22)$$

Recalling (7.13)_{2,3}, we write the constitutive equations for $\underline{p}^1, \underline{p}^2$ in the forms

$$\underline{p}^1 = D_4 \underline{v} + \underline{m}^1 , \quad \underline{p}^2 = D_7 \underline{v} + \underline{m}^2 , \quad (7.23)$$

so that

$$\underline{p}^1 \cdot \underline{n} = \underline{m}^1 \cdot \underline{n} , \quad \underline{p}^2 \cdot \underline{n} = \underline{m}^2 \cdot \underline{n} \quad \text{on } \partial\mathcal{R} , \quad (7.24)$$

in view of (7.22).

Consider now an initial boundary-value problem characterized by the differential equations (7.21) with $s_1 = s_2 = 0$. We assume that the dependent variables α, β are: (i) of class C^2 with respect to \underline{x} and of class C^1 with respect to t in the open region \mathcal{R} for $t \geq 0$; and (ii) of class C^1 with respect to \underline{x} and of class C with respect to t in the closed region $\mathcal{R} \cup \partial\mathcal{R}$ for $t \geq 0$. In addition, we assume the initial and boundary data

$$\alpha = 0 , \quad \beta = 0 \quad \text{in } \mathcal{R} \cup \partial\mathcal{R} \quad \text{for } t \geq 0 ,$$

$$\alpha = 0 , \quad \beta = 0 \quad \text{on } \partial\mathcal{R}_1 \quad \text{for } t \geq 0 , \quad (7.25)$$

$$\left. \begin{array}{l} \underline{p}^1 \cdot \underline{n} = \underline{m}^1 \cdot \underline{n} = 0 \\ \underline{p}^2 \cdot \underline{n} = \underline{m}^2 \cdot \underline{n} = 0 \end{array} \right\} \quad \text{on } \partial\mathcal{R} - \partial\mathcal{R}_1 \quad \text{for } t \geq 0 .$$

In order to establish uniqueness, from (7.21) and (7.25), we obtain

$$\begin{aligned} \frac{d}{dt} \int_R \frac{1}{2} (\delta_3 \alpha^2 + 2\delta_4 \alpha\beta + \delta_5 \beta^2) dv \\ = - \int_R [(D_{10}\alpha + D_{11}\beta)\beta - \underline{m}^1 \cdot \text{grad}(\alpha+\beta) - \underline{m}^2 \cdot \text{grad} \alpha] dv, \end{aligned} \quad (7.26)$$

which is an identity. Then, with suitable classes of functions α and β , the usual type of energy criteria for uniqueness follow from (7.26) provided

$$\begin{aligned} \delta_3 \alpha^2 + 2\delta_4 \alpha\beta + \delta_5 \beta^2 &\geq 0, \\ (D_{10}\alpha + D_{11}\beta)\beta &\geq 0, \end{aligned} \quad (7.27)$$

$$- \underline{m}^1 \cdot \text{grad}(\alpha+\beta) - \underline{m}^2 \cdot \text{grad} \alpha \geq 0,$$

for all temperature fields α, β . Further, with the help of (7.14) and (7.23), it follows from (7.27) that

$$\begin{aligned} D_5 + D_8 &\geq 0, \quad D_6 \geq 0, \quad 4D_6(D_5 + D_8) \geq (D_5 + D_6 + D_9)^2, \\ D_{10} &= 0, \quad D_{11} \geq 0, \quad \delta_3 \geq 0, \quad \delta_5 \geq 0, \quad \delta_3 \delta_5 \geq \delta_4^2, \end{aligned} \quad (7.28)$$

and we note that (7.28)₁ and (7.28)₆ are the same as the thermodynamic restrictions (7.19) and (7.20), respectively.

In order to illustrate some of the features of the equations (7.21) subject to the restrictions (7.28), we consider a simple example of heat conduction in an infinite stationary rigid porous solid bounded by the planes $x_1 = 0$, $x_1 = a$ and containing an incompressible viscous fluid at rest. At time $t = 0$, the temperature throughout the interior of the solid and fluid is constant and equal to $\bar{\theta}$. Let the temperature of the walls of the solid be changed to, and maintained at, another constant temperature. Then, when $0 < x_1 < a$, the quantities α, β satisfy (7.21)_{1,2} with $s_1 = s_2 = 0$ and are functions of t and x_1 . Also,

$$\alpha = 0, \quad \beta = 0 \quad (t=0; 0 < x_1 < a), \quad (7.29)$$

$$\alpha = \alpha_0, \quad \beta = 0 \quad (x_1 = 0, a; t \geq 0),$$

where α_0 is a constant. Following a routine method we look for solutions of (7.21)_{1,2} in the forms

$$\alpha = Ae^{\lambda t} \sin(n\pi x_1/a), \quad \beta = Be^{\lambda t} \sin(n\pi x_1/a), \quad (7.30)$$

where λ satisfies the quadratic equation

$$\begin{aligned} &(\delta_3 \delta_5 - \delta_4^2) \lambda^2 + \lambda [\{\delta_3 D_6 + \delta_5 (D_5 + D_8) - \delta_4 (D_5 + D_6 + D_9)\} \theta_n + \delta_3 D_{11}] \\ &+ (D_6 D_8 - D_5 D_9) \theta_n^2 + D_{11} (D_5 + D_8) \theta_n = 0 \end{aligned} \quad (7.31)$$

and

$$\theta_n = n^2 \pi^2 / s^2. \quad (7.32)$$

Recalling the conditions (7.28), we readily obtain the restrictions

$$\begin{aligned} &\delta_3 \delta_5 - \delta_4^2 \geq 0, \quad D_6 D_8 - D_5 D_9 \geq 0, \quad D_{11} (D_5 + D_8) \geq 0, \\ &\delta_3 D_6 + \delta_5 (D_5 + D_8) - \delta_4 (D_5 + D_6 + D_9) \geq 0, \quad \delta_3 D_{11} \geq 0 \end{aligned} \quad (7.33)$$

and then we conclude that the roots of (7.33) are in general of the form

$$\lambda = -\alpha_n, \quad \lambda = -\beta_n \quad (n=1,2,\dots), \quad (7.34)$$

$$\alpha_n > 0, \quad \beta_n > 0,$$

where α_n, β_n are unequal and real, or are of the form

$$\lambda = -\alpha_n \pm i\beta_n \quad (n=1,2,\dots), \quad (7.35)$$

where α_n, β_n are real and β_n are non-zero. Exceptional cases can arise but these can be dealt with similarly. The solution to the initial-boundary problem may now be completed in a usual way. We note, in particular, one result which follows from the solution, namely that

$$\alpha \rightarrow \alpha_0, \quad \beta \rightarrow 0 \quad \text{as } t \rightarrow \infty. \quad (7.36)$$

According to (7.36), which is an expected result, the temperatures in the fluid and solid tend to the same values as $t \rightarrow \infty$.

8. Further remarks.

We close this paper with some additional remarks concerning the present and previous procedures of studying the thermodynamics of mixtures of interacting continua with different constituent temperatures. First, we observe that the field equations resulting from momenta balances for each constituent involve only the mechanical fields while those obtained from balances of energy for each constituent involve both the thermal and the mechanical fields. In the traditional developments of thermomechanics, after the specification of constitutive equations, the former field equations yield a system of differential equations for the determination of deformations for each constituent while the latter is regarded as differential equations for the determination of the temperatures, after elimination of the external body forces with the use of the local equations of motion.* In contrast, the thermodynamical development of the present paper is such that the balances of entropy, which involve only the thermal fields, provide the differential equations for the temperatures in parallel with the fact that the differential equations for the deformations are derived from the balances of momenta. Consistent with this, the energy equation for the mixture as a whole (after the elimination of the external body forces and the external heat supplies) is employed as an identity for all thermomechanical processes; and, hence, it does not yield any new differential equation for temperatures or deformations. It is noteworthy that the energy equation for the mixture as a whole as used here provides all the essential results - other than those arising from inequalities - concerning the relationships between the constitutive response functions or functionals prior to any appeal to a second law of thermodynamics. In this sense, the inequalities (5.3) or (5.8) have been assigned a more subdued role relative to those of the conservation laws.

* It is understood that the differential equation for temperatures, as well as those for the deformations, contain also coupled terms.

In the spirit of the present paper, we could use the energy equations for each constituent as energy identities provided allowance is made for the interaction terms. However, this can be accomplished at the cost of introducing further variables requiring constitutive equations, and it does not appear likely to yield additional useful information.

We now turn to an entropy inequality of the Clausius-Duhem type for mixtures, namely

$$\sum_{\alpha=1}^v \frac{d}{dt} \int_{P_\alpha} \rho_\alpha \eta_\alpha dv - \sum_{\alpha=1}^v \int_{P_\alpha} \frac{\rho_\alpha r_\alpha}{\theta_\alpha} dv + \sum_{\alpha=1}^v \int_{\partial P_\alpha} \frac{\underline{q}^\alpha \cdot \underline{n}}{\theta_\alpha} da \geq 0, \quad (8.1)$$

which is proposed by Truesdell (11), and adopted in a number of recent papers on the subject, e.g., Green and Naghdi (5, 6, 7) and Craine et al. (2).

The inequality (8.1) may be regarded as a natural generalization of the Clausius-Duhem inequality for single phase continua and does lead to reasonable results in some special situations. For regions containing no surfaces of discontinuity, it follows from (8.1), (3.4) and (3.5) that

$$\sum_{\alpha=1}^v \rho_\alpha \xi_\alpha = \sum_{\alpha=1}^v \frac{1}{\theta_\alpha} \left[\theta_\alpha \left(\rho_\alpha \frac{D^\alpha \eta_\alpha}{Dt} + m_\alpha \eta_\alpha \right) - \rho_\alpha r_\alpha + \operatorname{div} \underline{q}^\alpha - \underline{p}^\alpha \cdot \operatorname{grad} \theta_\alpha \right] \geq 0 \quad (8.2)$$

for all thermo-mechanical processes. In previous papers on mixtures the external heat supplies r_α were eliminated from (8.2) with the help of the energy equations postulated for each constituent. Such a reduction cannot be effected here since in the present development we only have one energy equation. As a result, detailed comparison of the inequality (8.2) with that proposed in the present paper, namely (5.9), is difficult. However, some comparison can be made when all constituent temperatures θ_α are constrained to be equal to $\theta (> 0)$ as in (3.18). Then, using the energy equation (3.7) and the various definitions in §3, we may replace (8.2) by

$$\begin{aligned}
\theta \sum_{\alpha=1}^v \rho_{\alpha} \xi_{\alpha} &= - \sum_{\alpha=1}^v \left[\rho_{\alpha} \left(\frac{D^{\alpha} \psi}{Dt} + \eta_{\alpha} \frac{D^{\alpha} \theta}{Dt} \right) + m_{\alpha} \psi_{\alpha} + \frac{1}{2} m_{\alpha} \underline{u}^{\alpha} \cdot \underline{u}^{\alpha} \right. \\
&\quad \left. + \sum_{\alpha=1}^v (\underline{\mu}^{\alpha} \cdot \underline{v}^{\alpha} + \underline{T}^{\alpha} \cdot \text{grad } \underline{v}^{\alpha} - \underline{p}^{\alpha} \cdot \text{grad } \theta) \right] \\
&= \sum_{\alpha=1}^v (\rho_{\alpha} w_{\alpha} - \underline{p}^{\alpha} \cdot \text{grad } \theta) - \sum_{\alpha=1}^v \left[\rho_{\alpha} \left\{ \frac{D^{\alpha} (\eta_{\alpha} - \eta'_{\alpha})}{Dt} \right. \right. \\
&\quad \left. \left. + m_{\alpha} (\eta_{\alpha} - \eta'_{\alpha}) \right\} \right] \geq 0 .
\end{aligned} \tag{8.3}$$

For mixtures whose thermo-mechanical response is such that $\psi_{\alpha}, \eta_{\alpha}$ are independent of the set of variables (3.25), the specific Helmholtz free energies and the specific entropies reduce to $\psi_{\alpha} = \psi'_{\alpha}$, $\eta_{\alpha} = \eta'_{\alpha}$ and then (8.3) becomes

$$\theta \sum_{\alpha=1}^v \rho_{\alpha} \xi_{\alpha} = \sum_{\alpha=1}^v (\rho_{\alpha} w_{\alpha} - \underline{p}^{\alpha} \cdot \text{grad } \theta) \geq 0 . \tag{8.4}$$

If the variables $\psi_{\alpha}, \eta_{\alpha}, \underline{T}^{\alpha}, \underline{\mu}^{\alpha}, m_{\alpha}$ and hence $\rho_{\alpha} w_{\alpha}$ in (3.28)₁ do not depend on the temperature gradient $\text{grad } \theta$ and its history, then it readily follows from (8.4) that $\sum_{\alpha=1}^v \rho_{\alpha} w_{\alpha} \geq 0$ and this is the same as our inequality (5.9). On the other hand, provided $\sum_{\alpha=1}^v \underline{p}^{\alpha} \cdot \text{grad } \theta < 0$, the inequality (8.4) could allow $\sum_{\alpha=1}^v \rho_{\alpha} w_{\alpha}$ to be negative for some materials undergoing particular admissible processes.

Acknowledgement. The work of one of us (P.M.N.) was supported by the U.S. Office of Naval Research under Contract N00014-75-C-0148, Project NR 064-436, with the University of California, Berkeley (U.C.B.). Also, A.E.G. would like to acknowledge a visiting appointment in U.C.B. during 1976 and P.M.N. held a Senior Visiting Fellowship of the Science Research Council in the University of Oxford during 1975-76.

References

1. Atkin, R. J. & Craine, R. E., Continuum theories of mixtures: basic theory and historical development. *Quart. J. Mech. Appl. Math.* 29 (1976) 209.
2. Craine, R. E., Green, A. E. & Naghdi, P. M., A mixture of viscous elastic materials with different constituent temperatures. *Quart. J. Mech. Appl. Math.* 23 (1970) 171.
3. Green, A. E. & Naghdi, P. M., A dynamical theory of interacting continua. *Int. J. Engng. Sci.* 3 (1965) 231.
4. Green, A. E. & Naghdi, P. M., A theory of mixtures. *Arch. Rational Mech. Anal.* 24 (1967) 243.
5. Green, A. E. & Naghdi, P. M., On basic equations for mixtures. *Quart. J. Mech. Appl. Math.* 22 (1969) 427.
6. Green, A. E. & Naghdi, P. M., A mixture of elastic continua (in Russian). V. V. Novozhilov's Anniversary Volume, Academy of Sciences, U.S.S.R., 143, 1970; this is the same as Rept. No. AM-69-7, Division of Appl. Mech., University of California, Berkeley, April 1969.
7. Green, A. E. & Naghdi, P. M., The flow of fluid through an elastic solid. *Acta Mechanica* 9 (1970) 329.
8. Green, A. E. & Naghdi, P. M., On continuum thermodynamics. *Arch. Rational Mech. Anal.* 48 (1972) 352.
9. Green, A. E. & Naghdi, P. M., (a) On thermodynamics and the nature of the second law. To appear in *Proc. Royal Soc. (London)*; and (b) The second law of thermodynamics and cyclic processes. To appear in *J. Appl. Mech.*
10. Truesdell, C. & Toupin, R., The classical field theories. *Flügge's Handbuch der Physik*, Vol. III/1, p. 226 (Springer-Verlag, 1960).
11. Truesdell, C., Sulle basi della termodinamica delle miscele. *Rend. Accad. Nazionale Lincei* (8), 44 (1968) 381.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER 14 UCB/AM-77-8	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) 6 On Thermodynamics and the Nature of the Second Law for Mixtures of Interacting Continua		5. TYPE OF REPORT & PERIOD COVERED 9 Technical Report	
7. AUTHOR(s) 10 A. E. Green & P. M. Naghdi		8. CONTRACT OR GRANT NUMBER(s) 15 N00014-75-C-0148	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Mechanical Engineering University of California Berkeley, California 94720		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 064-436	
11. CONTROLLING OFFICE NAME AND ADDRESS Structural Mechanics Branch Office of Naval Research Arlington, Virginia 22217		12. REPORT DATE October 1977 Feb. 78	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 41	
		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Unlimited. <div style="border: 1px solid black; padding: 5px; display: inline-block;">DISTRIBUTION STATEMENT A Approved for public release; Distribution Unlimited</div>			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Mixtures of interacting continua, thermomechanics of multiphase continua, second law of thermodynamics for mixtures, balances of entropy, thermodynamic restrictions, restrictions on heat fluxes and internal energies for mixtures, the flow problem of (continued)			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This paper, which may be regarded as a continuation of a previous paper on thermodynamics of single phase continua, is concerned with a new approach to thermomechanics of multiphase continua and extends the previous ideas and procedure (Green and Naghdi 1977) to mixtures of interacting continua. In particular, it contains (a) a proposal of a new approach for obtaining restrictions on constitutive equations, (b) an appropriate mathematical statement (continued)			

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

400 426

19. Newtonian viscous fluid through a porous solid, effect of different temperatures of the fluid and the porous solid.

20. (continued)

of the second law for mixtures and (a) the nature of restrictions placed by the latter on constitutive results representing the thermomechanical behavior of mixtures with different constituent temperatures. Our point of departure is the introduction of balances of entropy and the use of a single energy equation for the whole mixture as an identity for all motions and all temperature distributions after the elimination of the external fields. This procedure is in contrast to the existing approach in most of the ~~current~~ literature on continuum theories of mixtures based on the use of a Clausius-Duhem type inequality (or similar entropy inequalities) for mixtures. Our interpretation of the second law is similar to that of the previous paper and leads us to postulate an inequality which reflects the fact that for every process associated with a dissipative mixtures, a part of the external mechanical work is always converted into heat and this cannot be withdrawn from the mixture as mechanical work. The restriction on the heat conduction vectors is considered separately and is confined to equilibrium cases in which heat flow is steady. Also, a restriction on the specific internal energies is derived when the mixture is in the state of mechanical equilibrium with all its constituents at a common spatially homogeneous temperature. The remainder of the paper deals with the constitutive results and thermodynamic restrictions for inviscid fluids, a fairly detailed consideration of the problem of an incompressible Newtonian viscous fluid flowing through a rigid porous solid whose temperature may be different from that of the fluid, as well as some additional remarks on the implication of the use of an entropy inequality of the Clausius-Duhem type for mixtures as contrasted with the thermodynamic restrictions resulting from the procedure proposed here and from our present interpretation of the second law.